

Report of RILEM TC 267-TRM phase 2

Optimization and testing of the robustness of the R3 reactivity tests for supplementary cementitious materials

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Report of RILEM TC 267-TRM phase 2: optimization and testing of the robustness of the R3 reactivity tests for supplementary cementitious materials

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Abstract The results of phase 1 of an interlaboratory test, coordinated by the RILEM TC 267-TRM “Tests for Reactivity of Supplementary Cementitious Materials” showed that the R³ (rapid, relevant, reliable) test method, by measurement of heat release or bound

water, provided the most reliable and relevant determination of the chemical reactivity of supplementary cementitious materials (SCMs), compared to other test methods. The phase 2 work, described in this paper aimed to improve the robustness of the test procedure

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and to develop precision statements for the consolidated test procedure. The effect of the pre-mixing and mixing conditions, and the impact of the mix design on the test method robustness were assessed and fixed for optimal conditions to carry out the R^3 heat release test. The effect of the drying step was evaluated to define the R^3 bound water test procedure in more detail. Finally, the robustness of the consolidated final test methods was determined by an interlaboratory study to define the precision statements.

Keywords Supplementary cementitious materials · Reactivity test · Robustness study · Heat release · Bound water

1 Introduction

One of the most efficient ways of reducing the CO₂ emissions of cement production is the partial substitution of Portland clinker by supplementary cementitious materials (SCMs) [1–3]. Most traditional SCMs such as coal combustion fly ashes and ground granulated blast furnace slags are in short supply globally relative to the demand for cement. This motivates the

identification of new SCMs or new combinations of conventional SCMs to continue decreasing the clinker factor of cement [4–6]. The assessment of the reactivity of SCMs is an essential step in determining the feasibility of their use in cement [7, 8]. The conventional way of measuring the reactivity is to carry out strength measurements on mortar at 28 days of hydration [9, 10]. However, this test requires a relatively large amount of material and is time consuming. Moreover, unreactive materials can pass such tests due to better packing or an increase of the hydration of clinker, e.g. by the filler effect [11, 12].

Accelerated reactivity tests were developed to assess the chemical reactivity of SCMs more directly. The RILEM TC 267-TRM (Tests for Reactivity of Supplementary Cementitious Materials) aimed to screen the performance of both standardized and novel reactivity test methods, and to recommend the most pertinent and robust reactivity test methods for evaluation by standardization committees. Several reactivity tests were evaluated by an interlaboratory study in phase 1 [13]. Eleven test materials were included in this testing phase, and the outputs of the tests were correlated with mortar relative compressive strength using 30% of cement substitution. The results of the Frattini test (EN 196–5) [14], the Chapelle test

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[15] and the modified Chapelle test (NF P18-513) [16] showed low correlation with mortar compressive strength when all SCMs were considered, and a very high variation between laboratories. The correlation with strength can be improved by excluding the slags from the range of SCMs tested. These tests measure the calcium consumption related with the pozzolanic reaction of SCMs, whereas slags are mainly latent-hydraulic and did not consume significant amounts of $\text{Ca}(\text{OH})_2$. The reactive silica test (EN 196–2) [17] also provided very low correlation with mortar strength. By far the highest correlation with mortar strength considering all SCM types was obtained for the R^3 test results [18] either by monitoring the heat release for 7 days by isothermal calorimetry or by determining the bound water of binder previously dried at 40 °C at 350 °C using an oven. As such, the R^3 test method was considered most promising and could be optimized to make it as universal, user-friendly and robust, i.e. repeatable and reproducible, as possible.

The objective of the phase 2 of the TC-267 TRM activities was to carry out an in-depth investigation of the impact of the experimental parameters of the R^3 test on the test results, in order to further improve the reproducibility between laboratories and the correlation with compressive strength development. This resulted in optimised and more detailed test procedures, which have been incorporated into the new ASTM standard C1897 adopted in 2020 [19]. Different steps and parameters were investigated, from the mix design of the R^3 test to the influence of the mixing conditions and the drying step procedure for the bound water test. Based on the results obtained, the final consolidated test methods were evaluated by an interlaboratory study (ILS) to establish the robustness of the methods and to develop precision statements.

2 Experimental

2.1 Materials

Six materials were used in this study, representing a wide range of SCM reactivities: two calcined clays, a siliceous fly ash, two ground granulated blast-furnace slags and a fine quartz. The calcined clay CC2 and slag S8 were used in the test method optimisation part of this study. These were substituted by calcined clay CC3 and slag S1 in the interlaboratory study testing

the consolidated test methods for logistic reasons. The chemical composition measured by X-ray fluorescence (XRF) spectroscopy and the physical properties of the test materials are shown in Table 1. The density was determined according to ASTM C188 [20] using isopropanol instead of kerosene. Table 2 indicates the mineralogical composition of the test materials determined by X-ray powder diffraction (XRD) combined with the Rietveld method using rutile as external standard. The particle size distribution was measured by laser diffraction using solvents (water or isopropanol) for the suspension following [21, 22].

2.2 Mortar compressive strength test

A clinker substitution level of 30 wt% was used for the mortars. Mortar bars were cast according to EN 196–1 [23]. Compressive strength measurements were carried out at 2, 7, 28 and 90 days of curing. Six participants carried out strength measurements, using six different commercially available CEM I 42.5 N/R cements. All the details of the Portland cements, with sulfate adjustment for the calcined clay blend, can be found in the phase 1 paper [13]. To minimise the variation due to the different cements, the relative compressive strengths were used to benchmark the outputs of the R^3 test. The relative strength $R_{\text{SCM,relative}}$ is calculated according to Eq. 1 from the absolute strength of the blended cement containing the SCM, R_{SCM} , and of the plain cement R_{PC} .

$$R_{\text{SCM,relative}}(\%) = \frac{R_{\text{SCM}} - R_{\text{PC}}}{R_{\text{PC}}} \times 100 \quad (1)$$

2.3 R^3 test (initial procedure)

2.3.1 R^3 test mix design

The R^3 test is designed to assess the chemical reactivity of an SCM in a system similar to a blended cement, but without the large variability brought by the clinker [18]. The mix design of the R^3 test is a model system composed of $\text{Ca}(\text{OH})_2$, the SCM along with calcite, alkali and sulfate, which are invariably present in real cements. The initial mix design of the R^3 is given in Table 3, modifications to which were tested in this paper. Characteristics of KOH, K_2SO_4 and calcite are detailed in the phase 1 study [13].

Table 1 Physical and chemical characteristics of the test materials. Omitted values (–) are below detection limits. Data were obtained by one laboratory

| Parameter | Calcined clay CC2 | Calcined clay CC3 | Slag S1 | Slag S8 | Fly ash SFA_R | Quartz Q |
|--------------------------------------|-------------------|-------------------|---------|--------------|-------------------|-------------------|
| Origin | India | India | France | India | Germany | Belgium |
| Part of the study | Optimisation | ILS | ILS | Optimisation | Optimisation, ILS | Optimisation, ILS |
| SiO ₂ (wt%) | 53.46 | 49.28 | 36.61 | 34.09 | 54.31 | 99.28 |
| Al ₂ O ₃ (wt%) | 34.88 | 42.28 | 12.21 | 19.87 | 22.72 | – |
| TiO ₂ (wt%) | 2.35 | 3.63 | 0.35 | 0.90 | 1.08 | 0.04 |
| MnO (wt%) | 0.01 | 0.01 | 0.14 | 0.09 | 0.05 | – |
| Fe ₂ O ₃ (wt%) | 3.39 | 2.22 | 0.85 | 0.45 | 10.28 | 0.03 |
| CaO (wt%) | 0.13 | 0.63 | 41.59 | 33.01 | 4.29 | – |
| MgO (wt%) | 0.09 | 0.03 | 7.18 | 9.73 | 1.47 | 0.05 |
| K ₂ O (wt%) | 0.23 | 0.06 | 0.28 | 0.84 | 2.08 | 0.10 |
| Na ₂ O (wt%) | 0.17 | 0.16 | 0.18 | 0.25 | 0.87 | 0.17 |
| SO ₃ (wt%) | 0.03 | 0.06 | 0.63 | 0.75 | 0.32 | 0.04 |
| P ₂ O ₅ (wt%) | 0.16 | 0.09 | 0.40 | 0.02 | 0.55 | 0.03 |
| L.O.I. 950 °C (wt%) | 5.00 | – | -0.03 | -0.37 | – | 0.15 |
| L.O.I. 1050 °C (wt%) | – | 2.26 | – | – | 1.32 | – |
| Density (g/cm ³) | 2.62 | 2.67 | 2.48 | 2.66 | 2.17 | 2.63 |
| Dv ₁₀ (µm) | 1.3 | 0.2 | 3.6 | 2.2 | 2.3 | 2.5 |
| Dv ₅₀ (µm) | 11.2 | 4.30 | 10.0 | 14.3 | 18.6 | 18.6 |
| Dv ₉₀ (µm) | 64.4 | 32.7 | 36.3 | 40.1 | 81.2 | 53.8 |

Table 2 Mineralogical composition of the test materials in wt%. Data were obtained by one laboratory

| Content (wt%) | Calcined clay CC2 | Calcined clay CC3 | Slag S1 | Slag S8 | Fly ash SFA_R | Quartz Q |
|------------------|-------------------|-------------------|---------|---------|---------------|----------|
| Anatase | 1.3 | 1.5 | – | – | – | – |
| Anhydrite | – | – | – | – | 1.3 | – |
| Calcite | – | – | 0.5 | 1.2 | – | – |
| Gehlenite | – | – | – | 6.2 | – | – |
| Hematite | 1.7 | 0.9 | – | – | 1.5 | – |
| Kaolinite | 12.0 | 5.3 | – | – | – | – |
| Magnetite | – | – | – | – | 1.4 | – |
| Mellilite | – | – | 0.3 | – | – | – |
| Mullite | – | 12.0 | – | – | 11.6 | – |
| Illite/Muscovite | 2.0 | – | – | – | – | – |
| Quartz | – | 0.8 | – | 0.5 | 8.8 | 99.8 |
| Rutile | 8.0 | 1.3 | – | – | – | – |
| Spinel | – | – | – | 0.4 | – | – |
| Amorphous | 75.0 | 78.0 | 99.2 | 91.8 | 75.0 | 0.2 |
| Sum | 100.0 | 99.8 | 100.0 | 100.1 | 99.5 | 100.0 |

The initial experimental procedure consisted of weighing all the materials, which are then stored in

sealed containers. The solid part is gently mixed by hand for 2 min. All components of the mix, as well as



the calorimetry ampoules, caps and pipettes are then stored at 40 °C overnight prior to casting. The solid and liquid parts are then mixed at 1600 rpm for 2 min using a propeller mixer.

2.3.2 R^3 heat release test

The first option to assess reactivity is to monitor the heat release during the first seven days of hydration at 40 °C using isothermal calorimetry. Before the test, the isothermal calorimeter is calibrated at this temperature. Ampoules of 20 ml with 9.4 g of water (to match the thermal mass of the pastes) are used as references. Immediately after casting, 15 g of fresh paste is inserted into the ampoules. The ampoules are then sealed and placed into the calorimeter. The cumulative heat release is calculated starting from 1.2 h after casting. This omits the first heat release peak, which is affected by the thermal equilibration of the sample within the calorimeter. This delay of 1.2 h was chosen based on a sensitivity analysis, which showed the highest reproducibility for this time. The cumulative heat values per gram of SCM at 3 or 7 days (72 or 168 h) are taken as indicators of the reactivity of the SCM.

2.3.3 R^3 bound water

If an isothermal calorimeter is not available to measure heat release, an alternative way of determining the chemical reactivity is to use an oven to measure the bound water content of the hydrated pastes. After mixing, the fresh pastes are cured at 40 °C in sealed plastic containers for 7 days. The pastes are then crushed, and pieces smaller than 2 mm to a total weight of about 10 g are placed in a crucible. The weight of the crucible is referred to as w_c . The crucible with the crushed pieces then undergoes a drying step. In the initial procedure it was dried in an oven at 105 °C for 2 h (but the drying procedure was changed as will be shown later). The weight including the crucible is recorded as w_0 . About 5 g of the dried

sample is heated at 350 °C for 2 h in a lab oven, followed by cooling in a desiccator (no vacuum) for 1 h over silica gel. The weight of the sample and the crucible is taken as w_t . The exposure time to ambient conditions between the moment the sample leaves the desiccator and the measurement of its weight is to be as short as possible. The amount of bound water is obtained according to Eq. 2, from the weight loss between drying and 350 °C, normalized by the weight of dried sample. The weight loss corresponds to the dehydration of the main hydration products. The bound water is directly used as indicator for the reactivity of the SCM.

$$\text{H}_2\text{O}_{\text{bound,dried}} = \frac{w_0 - w_t}{w_0 - w_c} \times 100 \quad (2)$$

2.4 Steps and parameters of procedures investigated

The steps and parameters of the procedures that were investigated were (these are also shown schematically in Fig. 1):

- **Premixing of the dry ingredients:** either shaking the solid part for 2–5 min by hand to achieve a uniform colour (hand method: h) or using a powder blender mixer, such as a Turbula device, for 5 min aiming to better homogenize the powder by blending in three dimensions (Turbula method: t)
- **Mixing conditions of the pastes:** the mixing of the powder with the solution was carried out using a high-shear overhead propeller blade mixer rotating at 1600 rpm for 2 min (Mechanical mixing: M) or hand-mixing using a spatula for 2 min (Hand mixing: H)
- **Use of a water bath, to maintain temperature during mixing and casting:** After taking the powder and solution cups from the oven at 40 °C, the mixing was carried out either at room temperature or by use of a water bath at 40 °C to immerse and heat the cup during the mixing (WB)

Table 3 R^3 model initial mix design

| Components | SCM | Ca(OH) ₂ | Deionized water | KOH | K ₂ SO ₄ | Calcite |
|------------|-------|---------------------|-----------------|------|--------------------------------|---------|
| Mass (g) | 11.11 | 33.33 | 60 | 0.24 | 1.20 | 5.56 |

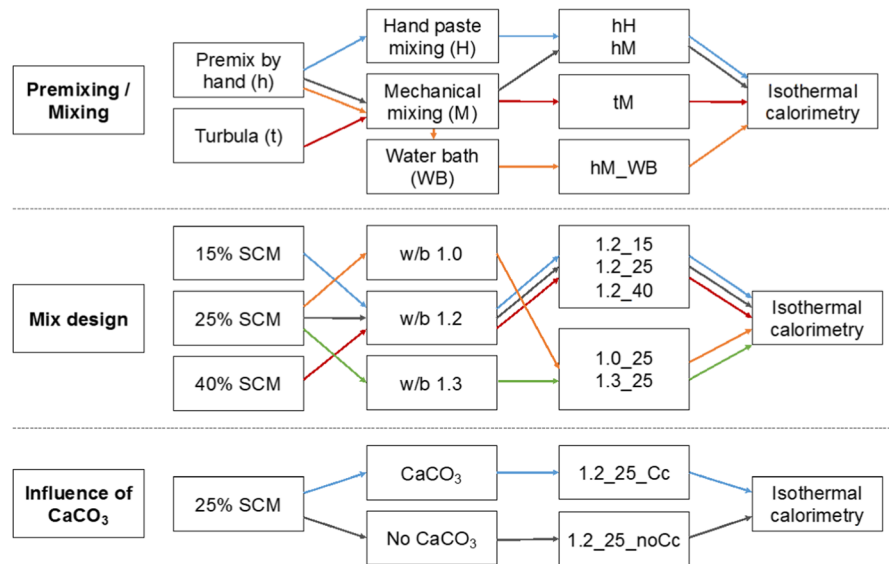


Fig. 1 Flowchart of the work plan for R^3 heat release testing

• **Proportions of ingredients in the mix design.**

The test material part was varied from 15 to 40 wt.% of the total mass of $\text{Ca}(\text{OH})_2$ and test material. Moreover, the water to binder mass ratio was also varied from 1.0 to 1.3 to control the effects on workability and the collected signal of different SCMs. The influence of CaCO_3 on the heat release was also investigated. The different mix design variations are summarized in Table 4. The above parameters have effect on both measurement methods, but were assessed here by the heat release method, due to its ease of use and greater precision.

In addition to the general parameters for each of the steps described in the procedure, the effect in the results when adopting the following testing conditions during the bound water test procedure were also investigated:

- **drying step** after crushing the R^3 paste in fine pieces (< 3 mm):
 - o 105°C (initial method): 2 h to reach a stable weight
 - p 50°C: 24 h to reach a stable weight
 - q 40°C: 48 h or 24 h to reach a stable weight
 - r Solvent exchange: 10 g of crushed pieces were immersed in 100 mL of isopropanol for 7 days. The solvent was renewed after 3 h, and 1, 2 and 4 days. The crushed pieces were

then stored under vacuum for at least 2 days before the oven test.

- **cooling time in desiccator:** 15 and 30 min, 1 and 2 h, 2 and 7 days.
- **exposure time to ambient conditions** once the samples are taken out of the desiccator before being weighed was studied, with a reference mass measurement after 30 s of exposure.

2.5 Data treatment

The correlation between the relative compressive strength of mortar and the outputs of the R^3 test was based on a linear regression. The quality of the correlation was indicated by the regression coefficient, R^2 .

The interlaboratory reproducibility was assessed by determining the coefficient of variation (CV_i), which was obtained according to Eq. 3. It considers the standard deviation (σ_i) and the difference between the averages (\bar{x}_i) of the SCM i and the quartz reference (\bar{x}_Q) results. The higher the coefficient of variation, the lower the reproducibility between laboratories.

$$CV_i(\%) = \frac{\sigma_i}{\bar{x}_i - \bar{x}_Q} \times 100 \quad (3)$$

Table 4 Variations in the R^3 mix design. The mix 1.2_25 corresponds to the initial mix design in Table 3

| Label: w/b_SCM% | SCM (wt%) | w/b* | SCM (g) | Ca(OH) ₂ (g) | Deionized water (g) | KOH (g) | K ₂ SO ₄ (g) | Calcite (g) |
|-----------------|-----------|------|---------|-------------------------|---------------------|---------|------------------------------------|-------------|
| 1.2_15 | 15 | 1.2 | 6.67 | 37.77 | 60 | 0.24 | 1.20 | 5.56 |
| 1.2_25 | 25 | 1.2 | 11.11 | 33.33 | 60 | 0.24 | 1.20 | 5.56 |
| 1.2_40 | 40 | 1.2 | 17.78 | 26.66 | 60 | 0.24 | 1.20 | 5.56 |
| 1.0_25 | 25 | 1.0 | 11.11 | 33.33 | 50 | 0.24 | 1.20 | 5.56 |
| 1.3_25 | 25 | 1.3 | 11.11 | 33.33 | 65 | 0.24 | 1.20 | 5.56 |
| 1.2_25_noCc | 25 | 1.2 | 11.11 | 33.33 | 60 | 0.24 | 1.20 | 0.00 |

*water to binder ratio (w/b) calculated as water to sum of all solids, reported value is rounded to first decimal

2.6 Interlaboratory robustness study

The interlaboratory study (ILS) was conducted in line with ASTM C802 [24]—that provides guidelines to design, execution and analysis of the data with the objective of developing precision statements for the R^3 test method (ASTM C1897 [14]). The precision statements provide acceptance values for the single-operator and multilaboratory standard deviations and difference limits expressed according to ASTM C670 [25].

Based on the optimization test program results, critical conditions were identified and specified in a consolidated R^3 test method used for the ILS within RILEM TC 267-TRM. Both R^3 measurement techniques (i.e. hydration heat and bound water determinations) were tested and evaluated separately in the ILS.

In the ILS, three materials, i.e. one ground granulated blast furnace slag (S1), one coal combustion fly ash (SFA-R) and one calcined clay (CC3) were tested. These materials covered a range of characteristics typical for materials used in practice. 11 laboratories tested the materials for hydration heat, and 13 laboratories measured bound water according to the test method. All test determinations were carried out in triplicate. As such, the ILS program comprises ILS data on two material characteristics, hydration heat and bound water reported by $p = 11$ and $p = 13$ laboratories, respectively; $q =$ three materials; and $n =$ three replicate test determinations per material. As a consequence, the ILS involves 33 and 39 degrees of freedom for single-operator standard deviation for measurement of hydration heat and bound water. The ILS complies with the ASTM C670 [25] and ASTM C802 [24] criteria of involving at least 30 degrees of

freedom for single-operator standard deviation and at least 10 laboratories for both characteristics. The data treatment and the development of precision statements followed the ASTM C802 and ASTM C670 guidelines, respectively.

3 Results

3.1 Influence of premixing and mixing conditions and use of water bath

The results obtained from four participants are shown in Fig. 2 for the different SCMs. The error bar indicates the maximum deviation between the participants, in this case for the calcined clay sample at 7 days. The averaged cumulative heat release shows very similar trends for fly ash and slag independent of the premixing conditions and the mixing conditions adopted. Slight differences are observed for the calcined clay. These differences as well as the larger variation on the results (error bar), are likely explained by the compositional heterogeneity of the calcined clay materials. The calcined clay materials were obtained from batch-scale pilot calcination trials. Therefore, they may not have the same level of homogeneity as the other materials which were commercial products from continuous industrial processes. Moreover, very similar heat release is monitored for the samples that were manually-premixed and mechanically-mixed with or without the use of a water bath under the cup during the mixing.

The coefficients of variation were determined based on the cumulative heat values measured at 0.5 d, 1 d, 3 d and 7 d of testing. The results are shown in Fig. 3. For all combinations of premixing and mixing

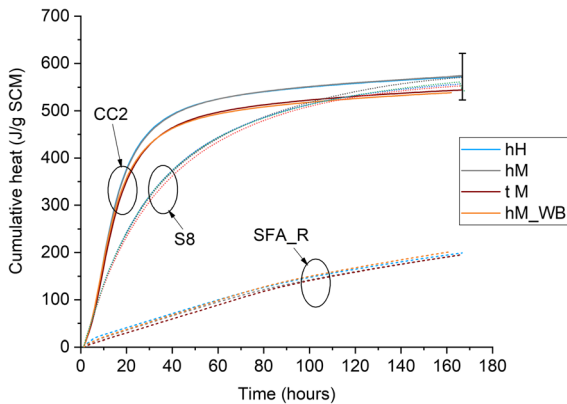


Fig. 2 Cumulative heat release averaged on four labs for the R^3 pastes using various pre-mixing procedures of powders and mixing conditions. The first letter of the coding corresponds to the premixing conditions: by hand (*h*) or using the Turbula mixer (*t*). The capital letter refers to the mixing conditions: by hand (*H*) or mechanical (*M*). The water bath (*WB*) is used only for manual premixing and mechanical mixing. The error bar indicates the highest deviation obtained, in this case for the calcined clay sample at 7 days for the hM combination

conditions, the coefficient of variation decreased with the increase of the testing duration, i.e. the highest reproducibility is obtained after 7 days of testing. Mechanical premixing and mixing gave slightly higher reproducibility at an early age, but all combinations gave very similar coefficients of variation at 7 days. The regression coefficient based on the heat release at 7 days is very similar for all pre-mixing and mixing combinations. Thus, the final protocol was chosen to be as practical and user-friendly as possible. The Turbula for the pre-mix and the use of the water bath were discarded, since they add extra complexity to the protocol without improving the correlation with mortar strength nor the reproducibility of the experiment. Manual premixing combined with mechanical mixing was retained.

3.2 Influence of mix design

The influence of the SCM content in the initial mix and the water to binder ratio is shown in Fig. 4, based on the results of five participants. Data for pastes containing fly ash, slag or calcined clay are shown. The relative cumulative heat release per gram of SCM increased with decreasing SCM content in the paste. This means that it would be best to compare and rank SCMs using pastes with lower SCM contents.

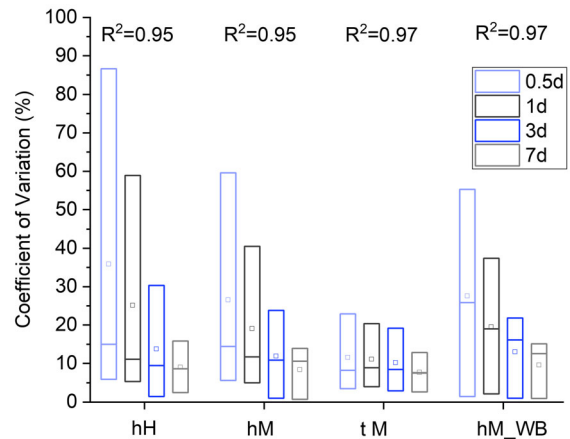


Fig. 3 Coefficient of variation and correlation coefficient for the premixing and mixing combinations based on the R^3 heat release outputs of four laboratories. The first letter of the coding corresponds to the premixing conditions: *h* for premix by hand, *t* for Turbula. The capital letter refers to the mixing conditions: by hand (*H*) or mechanical (*M*). The water bath (*WB*) is used only for manual premixing and mechanical mixing

However, in absolute terms of heat per gram of paste, the heat is the lowest for pastes the lowest SCM content. The heat release is similar for the three water to binder ratios used in this study, except for the slag sample which showed a slightly higher reactivity in the increase of the water content.

The coefficients of variation and the regression coefficients based on the data in Fig. 4 for all SCMs are shown in Fig. 5 for the different mix designs. With the highest paste SCM content, the regression coefficient was the lowest at 0.88, partly due to the complete consumption of portlandite during the reaction, for example in case of CC2 [18]. The R^2 value increased to 0.98 and 1.00 for the systems with 25% and 15% of SCM, respectively. However, the system with the lowest SCM content showed the highest coefficient of variation, due to the lower signal to noise ratio (i.e. the absolute heat release per gram of paste). The best conditions should allow an excess of $\text{Ca}(\text{OH})_2$ for the characterization of the reactivity of the SCM but also the monitoring of the highest signal possible from the SCM. The system with the 25% SCM content therefore provides the best compromise between obtaining high reproducibility and ensuring that the reaction of the SCM is not limited by depletion of $\text{Ca}(\text{OH})_2$. The range of water to binder ratios assessed does not significantly influence the regression coefficient. The coefficient of variation was slightly higher

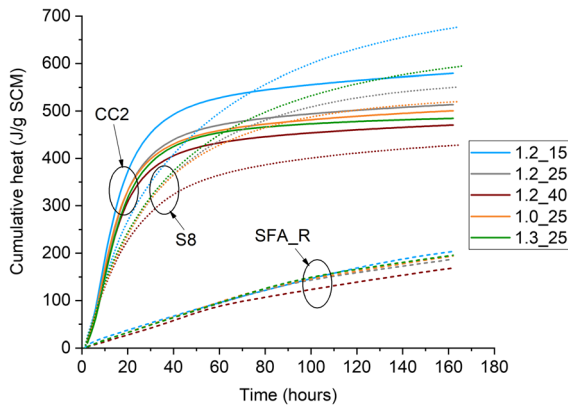


Fig. 4 Cumulative heat release averaged on five participants for the R^3 pastes with various SCM content and water to binder ratio. The first number indicates the water to binder ratio (from 1.0 to 1.3) and the second indicates the SCM content in the mix design (from 15 to 40%)

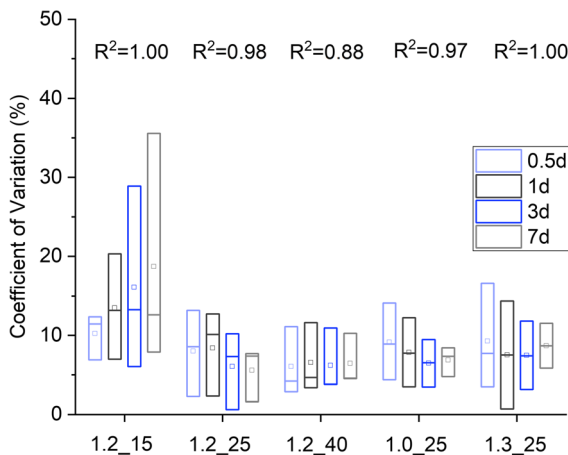


Fig. 5 Coefficient of variation (CV) and 28 day relative strength correlation coefficient (R^2) of the cumulative heat for the different SCM content and water to binder ratio used in the mix design, based on the outputs of five participants

for the highest water to binder ratio, likely due to dilution causing a lower signal to noise ratio. The use of 1.0 as water to binder ratio leads to insufficient workability for SCMs with a high water demand, such as calcined clays or silica fume. Thus, the SCM to $\text{Ca}(\text{OH})_2$ mass ratio of 1:3 (25%) and water to binder ratio of 1.2 were kept for the final protocol.

The influence of calcite in the initial mix design was tested by one laboratory and the results are shown in Fig. 6. The heat release was slightly lower in the presence of calcite in the system. However, the differences are within the range of error. The R^2

values for the heat values at 7 days for the systems with and without calcite were 0.93 and 0.94, respectively. Since the correlation is not affected by the presence of calcite, calcite was kept in the final protocol. The incorporation of calcite was considered also to add robustness in the case of non-ideal conditions, where there may be some carbonation of the $\text{Ca}(\text{OH})_2$. Moreover, the presence of calcite is also representative of the situation of most commercial cements.

3.3 Influence of drying step for R^3 bound water test

Figure 7 shows the amount of bound water for the different drying treatments, based on the results obtained by seven laboratories. The amount of bound water decreased with the increase of temperature for the different oven drying conditions. A higher temperature led to a higher evaporation of water in the sample prior to bound water testing. Thus, the remaining bound water measured afterwards at 350 °C was lower. The solvent exchange with isopropanol retained most bound water in the sample, but showed higher variation between the laboratories, particularly for SFA_R and S8 samples.

Figure 8 shows the coefficient of variations and the correlation coefficients to the 28 day relative strength for the different methods of drying. The use of 105 °C

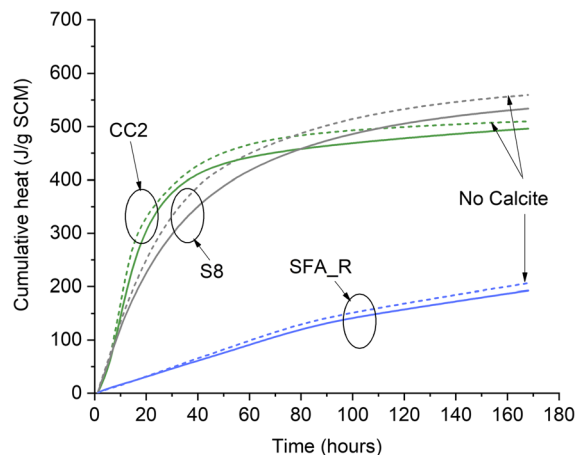


Fig. 6 Cumulative heat release for the R^3 pastes with or without calcite in the initial mix design. Dashed lines refer to mixes without calcite, and solid lines refer to mixes with calcite. The range of error is similar to Fig. 2. Results were obtained by one laboratory

as drying temperature led to a significant increase in the inter-laboratory variability. Despite the shortest drying time, the drying at 105 °C was abandoned due to poor reproducibility and the excessive removal of water from the hydrates. Solvent exchange showed the highest correlation coefficient, but also poor reproducibility and a lengthy procedure. The difference between 40 °C and 50 °C drying is not significant in terms of reproducibility. The drying at 40 °C gives a slightly higher correlation with 28-day strength. Thus, the drying at 40 °C was chosen for the final protocol. It also enables to use the same oven for curing the specimens and drying the crushed pastes.

The possibility of reducing the duration of the drying step at 40 °C from 48 to 24 h was investigated by one participant. The results in Fig. 9 indicate very similar values of bound water for both durations. Thus, the duration of the drying step can be shortened to 24 h without impacting the results and the correlation with strength. Drying at 40 °C for 24 h was retained for the final protocol.

Figure 10 shows the influence of the cooling time in a desiccator on the bound water. This part of the study was carried out on the same types of SCMs, but the calcined clay and the slag used were different. The bound water values did not vary with the cooling time. The crucibles were completely cooled down after 1 h in a desiccator. Thus, 1 h cooling time was kept in the final protocol, which is relatively short while helping to ensure robust results.

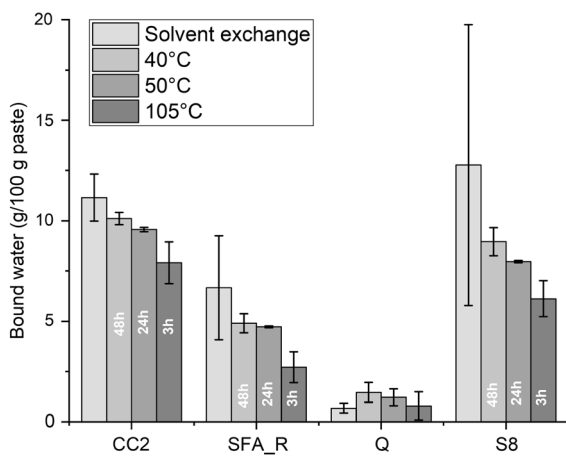


Fig. 7 Bound water content averaged over seven laboratories using solvent-exchange or oven at 40 °C, 50 °C or 105 °C for the drying step for the R³ pastes

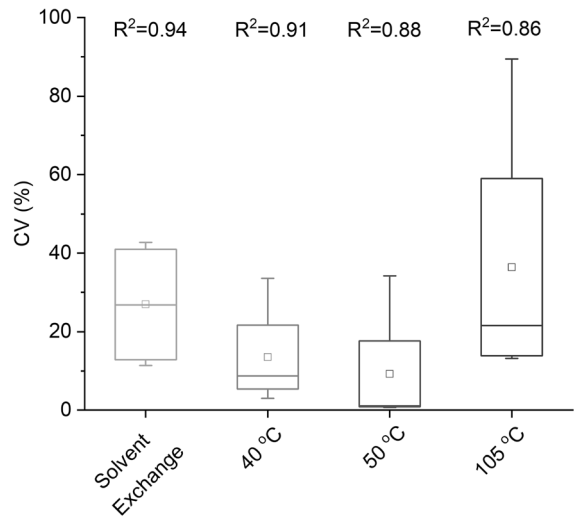


Fig. 8 Coefficient of variation (CV) and 28 day relative strength correlation coefficient (R^2) of the bound water determination using solvent exchange or an oven at 40 °C, 50 °C or 105 °C for the drying step. Results are averaged over seven participants

The influence of the exposure to ambient conditions on the samples is shown in Fig. 11. The exposure to the air led to a decrease of the calculated bound water values. This is due to the samples absorbing moisture from the air and there may also be some carbonation of the $\text{Ca}(\text{OH})_2$. Both caused an increase of the mass of the dried samples with the exposure time. Measurement of the sample mass within 10 min of exposure

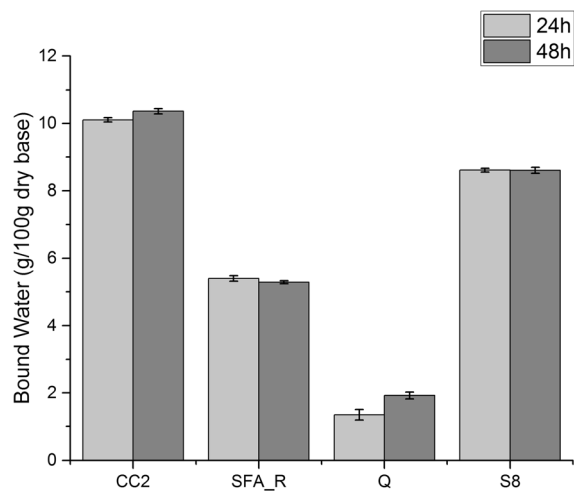


Fig. 9 Amount of bound water determined for the four SCMs using 24 h or 48 h for the drying step at 40 °C, results based on one participant

led to standard deviation values lower than 5% of the bound water values. Thus, a maximum exposure time of 10 min was added to the final protocol to minimise the impact of moisture absorption and carbonation.

3.4 Interlaboratory robustness study results

The data reported by the participating laboratories for hydration heat and bound water are provided as supplementary information. Data consistency was checked according to ASTM C802 to identify outlier laboratories and materials in terms of reported averages and dispersion of replicate results. The data consistency check revealed issues with two laboratories that were traced back to either calculation errors or malfunctioning or calibration issues of the calorimeters used for the heat of hydration experiments. One laboratory repeated the test determinations, the results of the other laboratory were discarded. Incomplete data reports were not considered either. In total, data reports from 11 labs were retained for hydration heat determination and from 13 labs for bound water determination. The material data consistency check revealed significantly higher variance of lab averages for the CC3 material, as compared to the S1 material that showed similar average values. This is probably related to the inherent heterogeneity of the CC3 material. Nevertheless, the reported results for the CC3 material were retained in further calculations.

In the next step, the following were calculated for each material (not shown): the overall averages, the pooled single-operator variance, the variance of

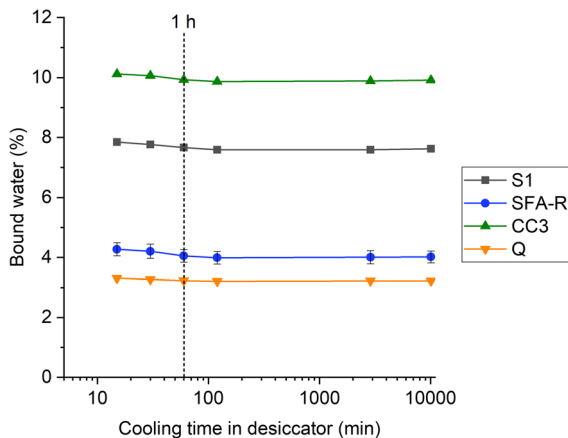


Fig. 10 Influence of the cooling time in desiccator on the bound water content. Results were obtained by one laboratory

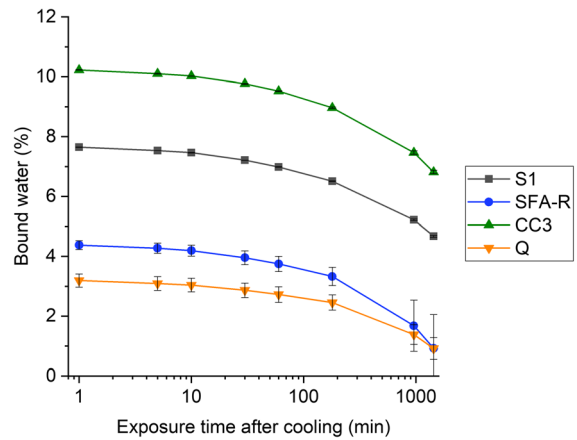


Fig. 11 Influence of the exposure time after cooling on the bound water content, results based on one participant

laboratory averages and the between laboratory component of variance of each determined characteristic. From these values, the single operator and multilaboratory standard deviations and coefficients of variation were derived. To develop the precision statements, the dependence of the calculated standard deviations and coefficients of variation on the determined characteristic value was checked by constructing cross-plots. In case of hydration heat, the standard deviations increased with increasing hydration heat, while coefficients of variation remained similar. For bound water, standard deviations were similar across the range of the reported bound water levels, while coefficients of variation decreased with increasing bound water values. Therefore, the coefficient of variation for the measurement of hydration heat and the standard deviation for the measurement of bound water are the most appropriate to include in the precision statements.

The laboratory averages, coefficients of variation for hydration heat measurements and standard deviations for bound water measurements for each test material are given in Table 5. It can be observed that values given for single-operator precision are similar for all materials, while multilaboratory precision values are significantly higher for CC3, supporting the supposition of greater material heterogeneity. Finally, from the ILS analysis results the precision statements and requirements were developed according to ASTM C670. Table 6 presents the determined single-operator and multilaboratory precision values and states the maximum accepted differences of the

Table 5 Summary table of calculated single-operator and multilaboratory standard deviations and coefficients of variation for each test material included in the ILS

| Material | Summary table | | | | | | | | |
|----------|----------------------|------------------------------|-----|----------------------|------------------------------|------|-------------------|--------------------------|------|
| | Hydration heat | | | | | | Bound water | | |
| | 3 day hydration heat | | | 7 day hydration heat | | | 7 day bound water | | |
| | Average | Coefficient of variation (%) | | Average | Coefficient of variation (%) | | Average | Standard deviation (wt%) | |
| | Single-operator | Multi-laboratory | | Single-operator | Multi-laboratory | | Single-operator | Multi-laboratory | |
| CC3 | 494.8 | 1.1 | 9.9 | 537.2 | 1.2 | 10.3 | 10.3 | 0.20 | 0.87 |
| S1 | 448.6 | 1.4 | 4.3 | 511.0 | 2.2 | 3.9 | 7.9 | 0.21 | 0.54 |
| SFA-R | 112.1 | 1.7 | 6.9 | 195.9 | 1.8 | 6.5 | 5.1 | 0.25 | 0.66 |

Table 6 R3 test method precision statements and maximum acceptable differences (d2s) of two properly conducted tests on the same material

| | Precision statements | | |
|---------------------------|------------------------------|------------------------------|--------------------------|
| | Hydration heat | | Bound water |
| | 3 day hydration heat | 7 day hydration heat | 7 day bound water |
| | Coefficient of variation (%) | Coefficient of variation (%) | Standard deviation (wt%) |
| Single-operator Precision | 2.0 | 2.3 | 0.18 |
| Single-operator d2s | 5.6 | 6.5 | 0.50 |
| Multilaboratory Precision | 7.1 | 7.0 | 0.46 |
| Multilaboratory d2s | 19.8 | 19.6 | 1.27 |

average of two properly conducted tests on the same material (d2s) by the same operator (single-operator) or by different laboratories (multilaboratory). The relatively large multilaboratory precision statements for the hydration heat measurements may indicate issues with the calorimeter calibration in some participating laboratories. It is expected that more detailed ILS instructions regarding calorimeter calibration, performance testing and baseline correction would enable to lower the d2s values.

4 Conclusion

The R³ test method for reactivity assessment of SCMs was improved by optimisation of process steps and mix design with respect to the test method robustness and the correlation of the result to the relative mortar strength benchmark.

- The pre-mix and mixing conditions studied did not play a major role in the correlation of the hydration heat at 7 days of hydration with mortar strength. The interlaboratory reproducibility was not affected by the type of pre-mix and mix procedure. Manual pre-mix and mechanical mixing were kept for the final protocol as the most pragmatic procedures.
- The use of a water bath to reduce the thermal loss during mixing did not affect or improve the correlation with strength. Since it adds extra complexity to the test procedures, the use of a water bath was not retained as part of the test method.
- The test material content corresponding to 25% of the Ca(OH)₂ content resulted in the highest correlation with strength measurement and the highest interlaboratory reproducibility; this ratio was therefore retained for the test method.



- The water to binder ratio was kept to 1.2 by mass for the consolidated procedure since it allows a proper mixing of the pastes.
- The presence of calcite in the R^3 mix design was retained. It led to a slightly lower heat release, but did not affect the correlation with mortar strength.
- For the bound water test, the drying at 40 °C provided the best compromise between the correlation with strength and the variance between laboratories. The selection of the temperature of 40 °C is also practical since the same oven can be used for the curing of the R^3 pastes and the drying of the crushed pieces.
- A cooling down to room temperature of 1 h in a desiccator is optimal. The time of exposure to the air before measuring the mass of the sample should not exceed 10 min to limit moisture sorption and carbonation.

The consolidated $R3$ test method for the determination of the chemical reactivity of an SCM by measurement of hydration heat and bound water was accepted as ASTM C1897-20 [14]. An interlaboratory study was conducted to define the test method precision and to provide precision statements for use of the test method. Single operator precision statements for both hydration heat and bound water measurements reflected the good repeatability of the test methods. The multilaboratory precision statement for bound water was found acceptable as well, only for the hydration heat the ILS provided rather low multilaboratory precision, which indicates that detailed instructions and strict compliance with calorimeter calibration requirements are a point of attention.

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Declarations The contents of this paper reflect the views of the authors, who are responsible for the validity and accuracy of presented data, and do not necessarily reflect the views of their affiliated organisations.

Conflict of Interest The authors declare that they have no conflict of interest.

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References

1. KL Scrivener, VM John, EM Gartner, 2016 Eco-efficient cements: potential, economically viable solutions for a low- CO_2 , cement-based materials industry, UNEP Report, United Nations Environment Programme, Paris, 50 pp.
2. Damtoft JS, Lukasik J, Herfort D, Sorrentino D, Gartner EM (2008) Sustainable development and climate change initiatives. *Cem Concr Res* 38:115–127
3. Schneider M (2019) The cement industry on the way to a low-carbon future. *Cem Concr Res* 124:105792
4. Snellings R (2016) Assessing, understanding and unlocking supplementary cementitious materials. *RILEM Tech Lett* 1:50–55
5. Juenger MC, Snellings R, Bernal SA (2019) Supplementary cementitious materials: new sources, characterization, and performance insights. *Cem Concr Res* 122:257–273
6. IEA 2018 International Energy Agency, Cement sustainability initiative & world business council for sustainable development: technology roadmap: low-carbon transition in the cement industry
7. Scrivener KL, Lothenbach B, De Belie N, Grunayert E, Skibsted J, Snellings R, Vollpracht A (2015) TC 238-SCM: hydration and microstructure of concrete with SCMs. *Mater Struct* 48:835–862
8. Snellings R, Scrivener KL (2016) Rapid screening tests for supplementary cementitious materials: past and future. *Mater Struct* 49:3265–3279



9. CEN/CENELEC, 2012 EN 450–1: Fly ash for concrete: definition, specifications and conformity criteria, CEN/CENELEC, Brussels, 34
10. ASTM C618–19, 2019 Standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete, ASTM International, West Conshohocken, PA
11. Kalina RD, Al-Shmaisani S, Ferron RD, Juenger MC (2019) False positives in ASTM C618 specifications for natural pozzolans. *ACI Mater J* 116:165–172
12. Berodier E, Scrivener K (2015) Evolution of pore structure in blended systems. *Cem Concr Res* 73:25–35
13. Li X, Snellings R, Antoni M, Alderete NM, Haha MB, Bishnoi S, Cizer Ö, Cyr M, De Weerd K, Dhandapani Y, Duchesne J, Haufe J, Hooton D, Juenger M, Kamali-Bernard S, Kramar S, Marroccoli M, Joseph AM, Parushar A, Patapy C, Provis JL, Sabio S, Santhanam M, Steger L, Sui T, Telesca A, Vollpracht A, Vargas F, Walkley B, Winnefeld F, Ye G, Zajac M, Zhang S, Scrivener K (2018) Reactivity tests for supplementary cementitious materials: RILEM TC 267-TRM phase 1. *Mater Struct* 51:151
14. CEN/CENELEC 2011 EN 196–5: Methods of testing cement - Part 5: Pozzolanicity test for pozzolanic cement, CEN/CENELEC, Brussels
15. Chapelle J (1958) Attaque sulfo-calcique des laitiers et des pouzzolanes. *Rev Matér Constr* 512:136–145
16. NF 2012 P18–513: Addition pour béton hydraulique - Métakaolin - Spécifications et critères de conformité, Paris, 19
17. CEN/CENELEC, 2013 EN 196–2: Methods of testing cement - Part 2: Chemical analysis of cement, CEN/CENELEC, Brussels, 73.
18. Avet F, Snellings R, Alujas Diaz A, Ben Haha M, Scrivener K (2016) Development of a new rapid, relevant and reliable (R3) test method to evaluate the pozzolanic reactivity of calcined kaolinitic clays. *Cem Concr Res* 85:1–11
19. ASTM C1897–20 2020 Standard test methods for measuring the reactivity of supplementary cementitious materials by isothermal calorimetry and bound water measurements, ASTM International, West Conshohocken, PA
20. ASTM 2017 C188–17: Standard test method for density of hydraulic cement, ASTM International, West Conshohocken, PA
21. Arvaniti EC, Juenger MCG, Bernal SA, Duchesne J, Courard L, Leroy S, Provis JL, Klemm A, De Belie N (2014) Determination of particle size, surface area, and shape of supplementary cementitious materials by different techniques. *Mater Struct* 48:3687–3701
22. Scrivener K, Snellings R, Lothenbach B (2016) A practical guide to microstructural analysis of cementitious materials. CRC Press, Boca Raton
23. CEN/CENELEC 2016 EN 196–1: Methods of testing cement - Part 1: Determination of strength, CEN/CENELEC, Brussels
24. ASTM 2014 C802–14: Standard Practice for Conducting an Interlaboratory Test Program to Determine the Precision of Test Methods for Construction Materials, ASTM International, West Conshohocken, PA
25. ASTM 2015 C670–15: Standard Practice for Preparing Precision and Bias Statements for Test Methods for Construction Materials, ASTM International, West Conshohocken, PA

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